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Effects of Anisotropic Coherency Strains on Intercalation in Phase-Separating Crystals

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Effects of Anisotropic Coherency Strains on Intercalation in Phase-Separating Crystals

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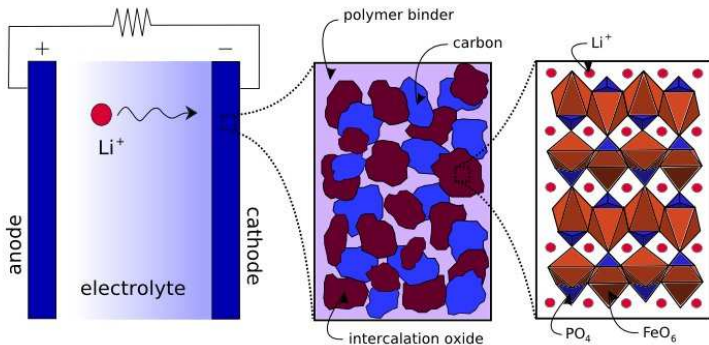
Massachusetts Institute of Technology

APS March Meeting

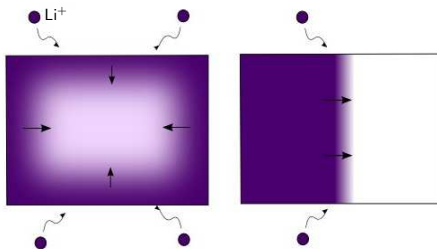
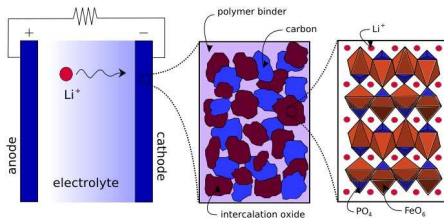
March 15, 2010

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Li^+ intercalation in Li_xFePO_4



Li^+ intercalation in Li_xFePO_4



phase-field formulation

- order parameter

$$c = [\text{Li}], \quad 0 < c < 1$$

- total free energy

$$\mathcal{F}[c] = \int_{\Omega} f(c, \nabla c, \dots) d\mathbf{x}, \quad \mathbf{x} \in \Omega$$

G.K. Singh, G. Ceder, M.Z. Bazant (2008)

energetic contributions

$$\mathcal{F}[c] \approx \int_{\Omega} \left\{ f_0(c) + \frac{1}{2} \nabla c \cdot \mathbf{K} \nabla c + \frac{1}{2} \mathbf{E} : \mathbf{T} \right\} d\mathbf{x}$$

energetic contributions

$$\mathcal{F}[c] \approx \int_{\Omega} \left\{ f_0(c) + \frac{1}{2} \nabla c \cdot \mathbf{K} \nabla c + \frac{1}{2} \mathbf{E} : \mathbf{T} \right\} d\mathbf{x}$$

$$f_0(c) = ac(1 - c) + k_B T [c \log(c) + (1 - c) \log(1 - c)]$$

energetic contributions

$$\mathcal{F}[c] \approx \int_{\Omega} \left\{ f_0(c) + \frac{1}{2} \nabla c \cdot \mathbf{K} \nabla c + \frac{1}{2} \mathbf{E} : \mathbf{T} \right\} d\mathbf{x}$$

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(enthalpy of mixing)

energetic contributions

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$$\mathcal{F}[c] \approx \int_{\Omega} \left\{ f_0(c) + \frac{1}{2} \nabla c \cdot \mathbf{K} \nabla c + \frac{1}{2} \mathbf{E} : \mathbf{T} \right\} d\mathbf{x}$$

\mathbf{K} – symmetric, positive-definite tensor

(gradient penalty)

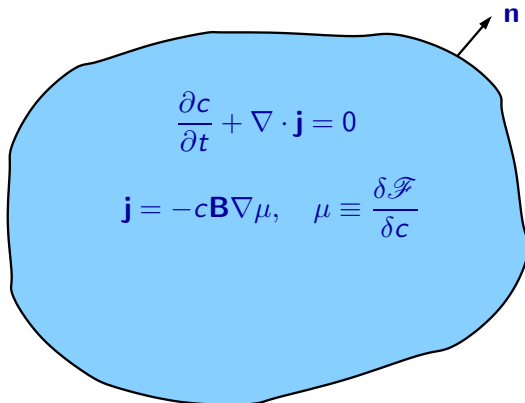
energetic contributions

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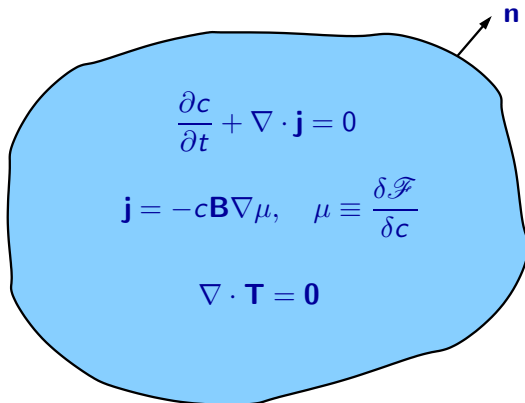
$$\mathbf{T} = \mathbf{C}\mathbf{E}, \quad \mathbf{E} = \frac{1}{2} \left(\nabla \mathbf{u} + \nabla \mathbf{u}^T \right) - c\mathbf{M}$$

(elastic energy)

governing equations

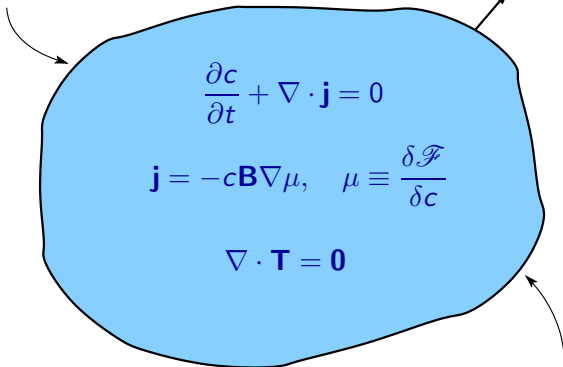


governing equations



governing equations

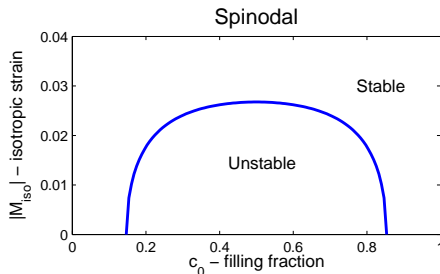
$$\mathbf{n} \cdot \mathbf{j} + R(\mu) = 0$$



$$\mathbf{n} \cdot (\mathbf{T} + P\mathbf{I}) = 0$$

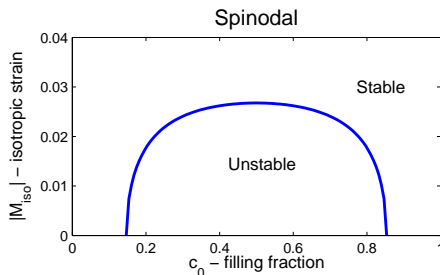
isotropic strain: $\mathbf{M} = M_{iso} \mathbf{I}$

$$\text{LSA: } c(\mathbf{x}, t) = c_0 + \tilde{c} e^{\sigma t + i \mathbf{q} \cdot \mathbf{x}}, \quad \mathbf{u} = \tilde{\mathbf{u}} e^{\sigma t + i \mathbf{q} \cdot \mathbf{x}}$$



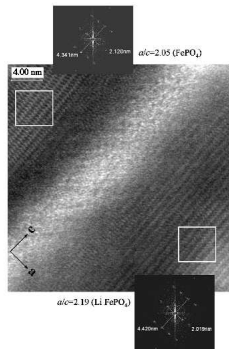
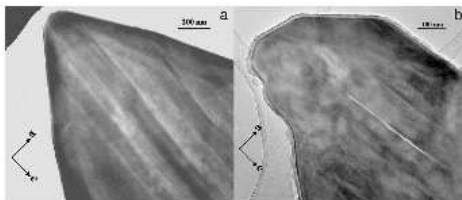
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strain suppresses phase-separation

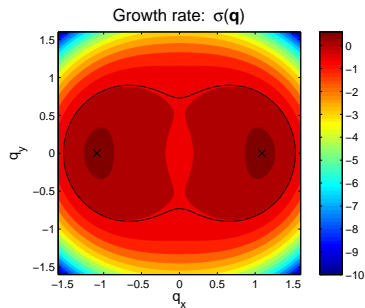
anisotropic strain



G. Chen, X. Song, T.J. Richardson (2006)

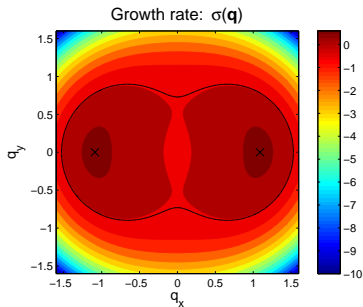
anisotropic strain

$$M_{11} = 0.05, M_{22} = 0.03, M_{33} = -0.02$$



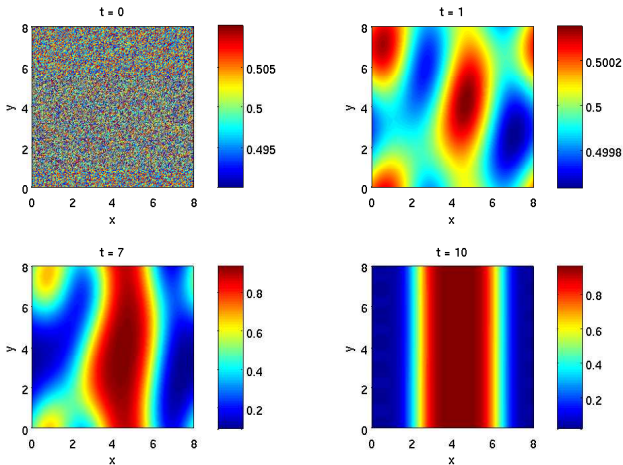
anisotropic strain

$$M_{11} = 0.05, M_{22} = 0.03, M_{33} = -0.02$$

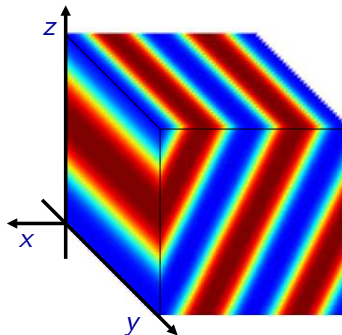


phase-separation occurs along direction of largest strain

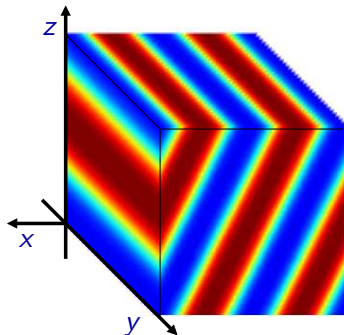
numerical simulations



numerical simulations



numerical simulations



skew induced by strain contraction

summary

- Extended model developed by Singh, Ceder and Bazant to include elastic effects from Li^+ intercalation in LiFePO_4
- LSA showed lattice mismatch strains to *suppress* spinodal decomposition (phase-separation)
- Phase-separation will occur along direction of *largest* strain with contraction induced skew
- Numerical simulations verify long-term dynamics

Thank You!